PART ONE

# THE STRUCTURE OF ISODURYLPHENYLVINYL ALCOHOL

PART TWO

# THE COUPLING ACTION OF THE GRIGNARD REAGENT

BY

JOSEPH WAYNE KNEISLEY

A.B., Miami University, 1939

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AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1943

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## Part One

# THE STRUCTURE OF ISODURYLPHENYLVINYL ALCOHOL

### Introduction

The effect of steric hindrance on the stability of enolic compounds has been studied intensively in recent years. Among the most interesting compounds investigated are certain derivatives of vinyl alcohol.

Heretofore the most remarkable stable vinyl alcohols synthesized had the structure $ArAr'=CHOH$ in which one or both of the aryl groups was mesityl. The object of the present research was to replace the mesityl radical with a group of similar hindering power. The most closely similar radical appeared to be the isoduryl; accordingly the specific objective of this work was to prepare and study 2-isoduryl-2-phenylvinyl alcohol.

### Experimental and Discussion of Results

Isodurylphenylvinyl alcohol was prepared by ozonization of 1-isoduryl-1-phenylethylene and by dehydration of 1-isoduryl-2-phenylethylene glycol by a mixture of hydrochloric and acetic acids.

The ethylene was prepared by the addition of methylmagnesium iodide to benzoylisodurene, an unusual reaction, since it involved 1,2 addition of a Grignard reagent to a hindered ketone. The glycol was obtained by the hydrogenation of isoduryl phenyl diketone, which, in turn, was produced by the oxidation of phenylacetoisodurene with selenium dioxide. The diketone was obtained in two isomeric forms. The yellow form is the true benzil, while the colorless modification no doubt has the superoxide or pseudobenzil structure.

The vinyl alcohol has been shown to possess the 2,2 diaryl structure, rather than a 1,2 form, by its unusual stability toward ketonization, and by comparison with the closely related compounds, mesitylphenyl-, dimesityl-, and di-(2,4,6-triiso-

propylphenyl) vinyl alcohols, which have been studied by Rabjohn,[1] Rowland,[2] and Ward.[3]

It was proposed to alter the vinyl alcohol substituents still further by replacing the hydrogen atom on the *alpha* carbon atom by the methyl group. This vinyl alcohol, 1-mesityl-1-phenyl-1-propen-2-ol, was to be prepared by enolization of the corresponding ketone, 1-mesityl-1-phenyl-2-propanone. The synthesis of the ketone began with the preparation of mesitylphenylacetic acid from mesitylene and mandelic acid in 85 per cent yield, using stannic chloride as a catalyst.[4] Treatment of the corresponding acid chloride with methylzinc iodide by the Blaise method[5] gave the desired ketone in 55 per cent yield. Distillation of mesitylphenylacetyl chloride in the presence of a trace of pyridine hydrochloride gave mesitylphenylketene in good yield. The ketene was transformed into its dimer upon standing in a stoppered flask.

All attempts to produce a stable enol from 1-mesityl-1-phenyl-2-propanone failed. However, when the ketone was treated with sodium methoxide in *n*-butyl alcohol at 70° for fifteen hours, mesitylphenylacetic acid was formed. This result indicated that a hydrogen atom from the methyl group had been enolized preferentially, and that the resultant enol formed a peroxide involving the methylene group. Cleavage of the peroxide resulted in the loss of a carbon atom, and the formation of mesitylphenylacetic acid.

It has been concluded that the hindrance of the mesityl radical on the *beta* carbon atom, which was expected to render the vinyl alcohol stable toward ketonization by hindering the return of the proton to that carbon atom, actually prevented the formation of the enol by reducing the mobility of the tertiary proton in the ketone to less than that of the primary proton from the methyl group. A similar conclusion was reached recently by Whitmore[6] in his observations of dineopentyl ketones.

The present work constitutes further evidence that hindrance about the *beta* carbon atom is the determining factor in the stability of vinyl alcohols.

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# Part Two

# THE COUPLING ACTION OF THE GRIGNARD REAGENT

## Introduction

Compounds containing active halogen atoms are coupled by aliphatic Grignard reagents in the manner of the Wurtz reaction. The influence of steric hindrance upon the coupling of di-*ortho*-substituted benzyl chlorides has been studied recently by Denton.[1] This investigation is a continuation of that work, and is concerned with the action of methylmagnesium iodide on 2,6-dimethyl-4-*t*-butylbenzyl chloride and *sym*-triisopropylbenzyl chloride.

## Experimental and Discussion of Results

2,6-Dimethyl-4-*t*-butylbenzyl chloride(I) and *sym*-triisopropylbenzyl chloride have been coupled by methylmagnesium iodide to the corresponding 1,2-diaryl ethanes in yields of 89 and 63 per cent, respectively. Alkylation of the benzyl chlorides by the Grignard reagent occurred simultaneously.

The benzyl chlorides were prepared by chloromethylation of the corresponding hydrocarbons. The chloromethylation of 1,3-dimethyl-5-*t*-butylbenzene(II) with formalin and hydrochloric acid gave only one benzyl chloride; hence it was assumed that substitution had taken place exclusively between the methyl groups. Appreciable amounts were always obtained of the side-product, di-(2,6-dimethyl-4-*t*-butylphenyl)methane. This compound would be expected to result from the condensation of I with the parent hydrocarbon II.

The reactivity of the halogen in the benzyl chloride I was further demonstrated by its reaction with ethanol to form

the ethyl ether, and by its reduction with zinc and alkali to 1,2,3-trimethyl-5-*t*-butylbenzene. Treatment of this hydrocarbon and 1,3-dimethyl-2-ethyl-5-*t*-butylbenzene with fuming nitric acid at 0° gave dinitro derivatives and, in addition, lower-melting substances which have been identified tentatively as trinitrates of the hydrocarbons.

## Summary

Methylmagnesium iodide has been found to couple 2,6-dimethyl-4-*t*-butylbenzyl chloride to the ethane in 89 per cent yield. Since benzyl chloride is coupled in only 75 per cent yield,[2] it is apparent that the *ortho* methyl groups not only offer no opposition to the condensation, but actually favor it.

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## VITA

The writer was born in Jeffersonville, Ohio on May 15, 1917. He attended the public school in Quincy, Ohio, and was graduated in May, 1935. From September, 1935 to June, 1939 he attended Miami University, where he was granted the Bachelor of Arts degree. In September, 1939 he entered the Graduate School of the University of Illinois where he held a teaching assistant in inorganic chemistry until June, 1941. During the years 1941-1943 he held University Fellowships.

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